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A FIXED BED COLUMN USING BAGASSE ASH FOR BRINE WASTEWATER TREATMENT FROM THE SUGAR REFINING PROCESS

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ABSTRACT

The objective of this current study was to determine and compare the characteristics and decolorization efficiencies of bagasse ash (BA) and granular activated carbon (GAC) in the treatment of brine wastewater (BWW). BA not only showed lower fixed carbon (45.8%) content than GAC (77.0%) but was also found to have a lower surface area (194 m^2/g) compared with GAC (211 m^2/g). The effect of flow rate, initial color of BWW and adsorbent bed depth on color removal were investigated and optimal conditions identified as a flow rate of 120 mL/min, original color of 2.00 and bed depth of 140 cm. The efficiency of BWW decolorization by BA and GAC was found to be related to the mesopore volume and surface area of the adsorbents. The effluent volumes required for decolorization to the target colour value of industry at 60%were determined as 36 and 157 L/kg of BA and GAC adsorbent, respectively. The chemical oxygen demand (COD) removal capacity of BA and GAC were 248 and 2,241 mL/L per one kilogram of adsorbent, respectively. The characteristics of the treated BWW sampled after passing through the BA column indicated that the developed adsorption process shows great prospect for the decolorization of brine effluents produced during brine recovery at an industrial scale, due to allowing the recovery and reuse of spent salt, as well as reducing the salt and water consumption of the process.

KEY WORDS : Bagasse ash, Brine wastewater treatment, Sugar refining process, Adsorption, Fixed bed column

INTRODUCTION

Owing to its utmost importance for the environment, agriculture and industry, water is one of earth's most precious natural resources (Voulvoulis, 2018). In conjunction with the steadily rising demand for fresh water as a result of the global population growth, the impending climate change threatens water supply and is likely to increase the occurrence and severity of drought periods in many parts of the world (Pongnam and Plermkamon, 2018). Therefore, reduction of water consumption as well as recycling of wastewater play a crucial role in ensuring the sustainability of human living, society and industries (Pongnam and Plermkamon, 2017; Voulvoulis, 2018).

In Thailand, the sugar industry represents one of the major industrial branches, as the country has become the second largest exporter of raw sugar in the world (Sukyai *et al*., 2016). In addition, the Thai government announced plans to increase the annual sugarcane production from 94up to 180 million tons until 2036 (Sukyai *et al*., 2016). Effective water management in this industrial branch remains therefore one of the key factors affecting sustainable resource utilization in the country. Consequently, the reduction of water consumption and emission of pollutants, as well as recycling and reuse of water

inside the sugar factories have been defined as a priority for all Thai sugar industries.

Wastewater treatment in sugar factories represents an important means to reduce the consumption of raw water from natural source (Cortés *et al*., 2010). The decolorization step in the sugar refining process generates substantial quantities of brine effluent during resin regeneration, which is characterized by caustic pH, high organic matter (colorants) content, high sodium and chloride ion concentration etc. Colorants mainly consist of melanins, melanoidines, caramels and polyphenols that originate from the sugar liquor (Hinkova *et al.,* 2002). The brine wastewater (BWW) typically has a chemical oxygen demand (COD) of 0.45-1.30 g/L and comprises approximately20-50 g/L total solid content, out of which 0.25-50 g/L are NaCl (Ngasan *et al.,* 2019; Wadley *et al.,* 1995). In order to recover the salt and allow its reuse in subsequent regeneration cycles, the brine effluent collected during the regeneration step is sent from the resin tank to a nano-filtration (NF) membrane unit. While then a no-filtration system can achieve up to 90% salt recovery when regenerated membranes are employed, the percentage of salt recovery usually declines after along-term use (Theoleyre *et al.,* 2012; Rein, 2007). This performance degradation is caused by the high concentration of dissolved and suspended solids in the brine effluentretarding or blocking the membrane surface, which is referred to as membrane fouling. To avoid permanent damage to the membrane due to this phenomenon, additional separation techniques need to be incorporated into the recovery process (Kushwaha *et al*., 2010; Ariono *et al*., 2016). For example, fouling in membrane bioreactors (MBRs) has been successfully reduced by use of nitrifying-enriched activated sludge (NAS). Moreover, the implementation of adsorption technology offers a promising alternative to remove organic matter and colourants during wastewater treatment (Doðan *et al*., 2004; Kushwaha *et al*., 2010 and Nure *et al.,* 2017). The combination of colorant adsorption and membrane separation couldhence increase the recovery of regenerated brine and effluent from the NF system and help to prevent pollution of the environment, either by reuse of spent brine or reduction of total brine wastewater production.

A recent study by Agarwal and Yadav (2016) demonstrated the possibility of utilizing bagasse fly ash (BFA) for the filtration of BWW with a recovery reaching 80% to 95% of the original system using nano- and RO membranes. Several other studies reported the use of activated carbon (AC) from bagasse bottom ash (Simaratanamongkol and Thiravetyan, 2010), unburnt carbon (Kaushik *et al.,* 2017) and bagasse fly ash (Nure *et al.,* 2017) to remove melanoidin from a synthetic melanoidin solution. AC from BFA was found to reduce the COD and remove color at a maximum adsorptive capacity for melanoidin of 124.8 mg/g. Furthermore, the adsorbent dose, contact time, pH and initial COD concentration were shown to affect the melanoidin adsorption performance (Nure *et al.,* 2017). Ngasan *et al.,* (2019) reported the possible utilization of treated fly ash for the removal of colorants from brine wastewater on a laboratory scale using a maximum dosage of 12% w/v treated fly ash.

Based on these encouraging findings, the current research aims to investigate the use of low-cost adsorbents derived from bagasse bottom ash in the decolorization of brine effluents from the brine recovery (membrane) system for improving the process of brine recycling in pilot scale applications. Therefore, the BWW decolorization efficiency of BA was studied in a pilot scale fixed bed column system and compared to a commercial adsorbent with regard to physical and chemical properties. The characteristics of the treated BWW were analyzed before and after passing through the BA column.

MATERIALS AND METHODS

Materials

The BA was collected from a Bio-power plant located in Chaiyaphum province, Thailand, washed to remove sand and dirt and screened through a 250 µm sieve. The sample was passed through a 1,180 µm sieve screen to remove unburnt material of large particle size. It was then washed with water until a pH of 7.0-7.2 was achieved and subsequently dried in anovenat 120 °C until complete dryness and stored in sealed plastic bags. Granular activated carbon (GAC), Norit®1240, produced by Norit using steam activation of select grades of coalwas obtained as reference material. BWW samples were collected directly in the brine recovery system (BRS) from a sugar refinery located in Chaiyaphum, Thailand.

Physical and chemical characterization of adsorbents

The particle size distribution, average diameter (D_n) and coefficient of variation (CV) of BA and GAC were measured using a CAMSIZER particle analyzer (Retsch GmbH, Germany). The bulk densities of the adsorbents were determined by the ASTM D 2854-09 method (Gholami *et al.*, 2014). Fixed carbon, ash, volatile and moisture contents were determined via thermogravimetric analysis (TGA) (Leco 701, USA), by measuring the rate of weight loss for each sample between 30 °C to 1,000 °C (Rodríguez-Díaz *et al.*, 2015). The carbon, hydrogen, nitrogen and sulfur (C, H, N, S) composition was analysed using a Perkin Elmer 2400 Series II CHNS/O Elemental Analyzer (Perkin Elmer Instruments, USA). Elemental composition of the sample was determined by atomic absorption spectrophotometer (AAS) (Khan and Qasim, 2008).

The surface area, pore volume and average pore size of BA and GAC were determined from the respective nitrogen adsorption isotherms using a BEL-sorp instrument and applying the Brunauer-Emmett-Teller (BET) method. Fourier Transform Infrared Spectroscopy (FTIR) (Bruker /Tensor 27-Hyperion, USA) was used to examine the functional groups present within the samples over a range of 400"4,000 cm^{-1}. The microscopic structure of BA was investigated via Scanning Electronic Microscopy (SEM) using a JEOL JSM-6010LV microscope (JEOL, USA).

Column preparation

The experimental set up used in the adsorption trials consisted of a stainless steel column (9 cm diameter, 140 cm height and approximately 9.69 Ltotal bed volume) fitted with filtersepta for carbon filtration placed at the bottom and the top of the column, as shown in Fig. 1. Cotton wool was used to cover the screen filters in order to prevent the loss of low particle size carbon material into the effluent water. BWW samples from the sugar refinery were continuously fed to the bottom of the packed column using a diaphragm pumpmodel IP66/NEM A4X (Watson-Marlow, Germany).

Decolorization of brine wastewater by bagasse bottom ash

The influence of flow rate, bed depth and initial $OD_{420\ nm}$ on the decolorization of BWW using BA were investigated. The column was packed with

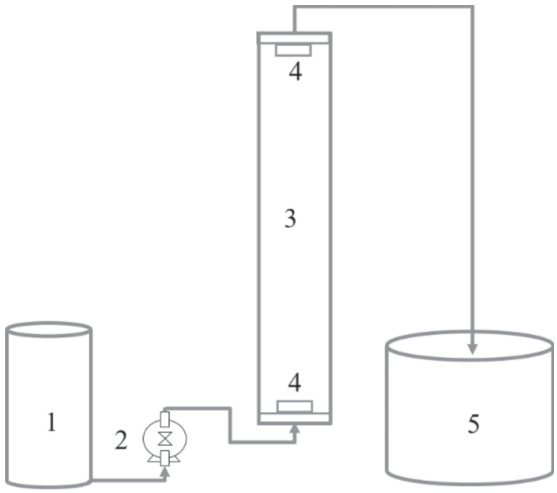

Fig. 1. Schematic representation of the pilotscale fixedbed continuous adsorption equipment used in this study;
1- feed tank, 2- pump, 3- column, 4-filter septafor carbon filtrationand 5- storage tank.

either 0.5, 1.0 or 2.0 kg of BA (equivalent to a bed depth of 35, 70 and 140 cm). The flow rate of the influent was adjusted to 120, 230 and 460 mL/min while the initial OD_{420nm} of the BWW was approximately 1.0, 2.0 and 7.0. The samples were collected before and after treatment in order to analyze the decolorization efficiency. Influent pumping and effluent collection were continued until color removal in the effluent sample could no longer be visibly discerned. All experiments were carried out at room temperature.

The ability of different adsorbents to decolorize BWW was analysed according to the method described by Ngasan *et al.* (2019). In brief, the wastewater samples were filtrated through a filter membrane (0.45 μm) before the percentage of colour removal was calculated by measuring the absorbance at λ_{max} of 420 nm using an ultraviolet (UV)–spectrophotometer (Helios-Alpha, Thermo Spectronic, USA). Samples with an absorbance above 1.0 were diluted with distilled water and compared with the initial value of the BWW. The percentage of colour removal was calculated according to Equation 1:

$$\% \text{ removal} = \left(\frac{Abs0 - Abst}{Abs0}\right) \times 100 \quad \ldots\ldots. (1)$$

where Abs_0 is the initial absorbance of the wastewater and Abs_t is the absorbance of wastewater at a specific time.

Breakthrough studies of brine wastewater treatment

Breakthrough studies for BWW decolorization were conducted to emulate the wastewater treatment process on an industrial scale. The column was therefore filled to its full capacity with either of the two adsorbents (BA and GAC) to a bed depth of 140 cm (2.0 kg for BA and 5.1 kg for GAC). Flow rate and initial $OD_{420\ nm}$ of the influent were maintained at 120 mL/min and 2.0, respectively. An $OD_{420\ nm}$ of the effluent above 0.8 units or color removal efficiency of 60% (representing the target value of the sugar factory) was defined as the breakthrough point.

Characterization of treated wastewater

The indicator values (I.V.) of treated wastewater samples from previous breakthrough experiments, defined as the colour difference ($OD_{420\ nm}$) between pH 9 and pH 4, were determined with the absorbance at λ_{max} of 420 nm (Clarke *et al*., 1986). The indicator value was calculated according to Equation 2.

$$\text{Indicator Value (I.V.)} = \left(\frac{OD420\ nm,pH\ 9}{OD420\ nm,pH\ 4}\right) \quad .. (2)$$

pH and electrical conductivity (EC) were measured with a pH meter and conductivity meter (Model PC700, Eutech Instruments, USA). The COD was measured using peptic device DRB 200, HACH, and spectrometer (DR5000 HACH, Canada) operating at 620 nm wavelength according to the American Standard method (AOAC2002) (Jahed *et al.*, 2014). Quantitation of heavy metals in BWW before and after the adsorption process was performed by Inductive Coupled Plasma Spectroscopy (ICP) (Shimadzu, Japan), according to Martin *et al*. (1992).

RESULTS AND DISCUSSION

Physical and chemical properties

The particle size distribution (PSD) of BA and GAC are shown in Fig. 2. The data regarding the D_n and coefficient of variation (CV) for BA and GAC presented in Table 1 clearly demonstrates that the CV of BA(160) is greater than that of GAC (37.7), while the $D_n$of BA and GAC are 364 µm and 1,062 µm, respectively. The PSD of the BA used in the present study was found similar to values reported previously for BA from South Africa and Brazil by Rodríguez-Díaz *et al.*, 2015. A PSD with a normal distribution facilitates column packing and can prevent critical pressure drops (Rodríguez-Díaz *et al.*, 2015; Karunarathne and Amarasinghe, 2013). Therefore, the smaller particle size of BA may result in greater susceptibility toinduce pressure drops in the fixedbed column compared to the commercial GAC sample, which displayed a rather normal PDS.

BA and GAC were analysed for volatile matter, fixed carbon and ash content in addition to elemental carbon, hydrogen, nitrogen and oxygen determination. The physico-chemical properties and elemental composition of BA and GAC are presented in Table 1. BA was found to containa lower amount fixed carbon (45.8%) than GAC (77.0%), while the ash content of BA (37.4%) was higher than that of GAC (9.7%). The elemental analysis revealed BA to comprise C, H, N, S contents of 47.02%, 2.04%, 0.30% and 0.03%, respectively, which is similar to results disclosed by Mary *et al.*

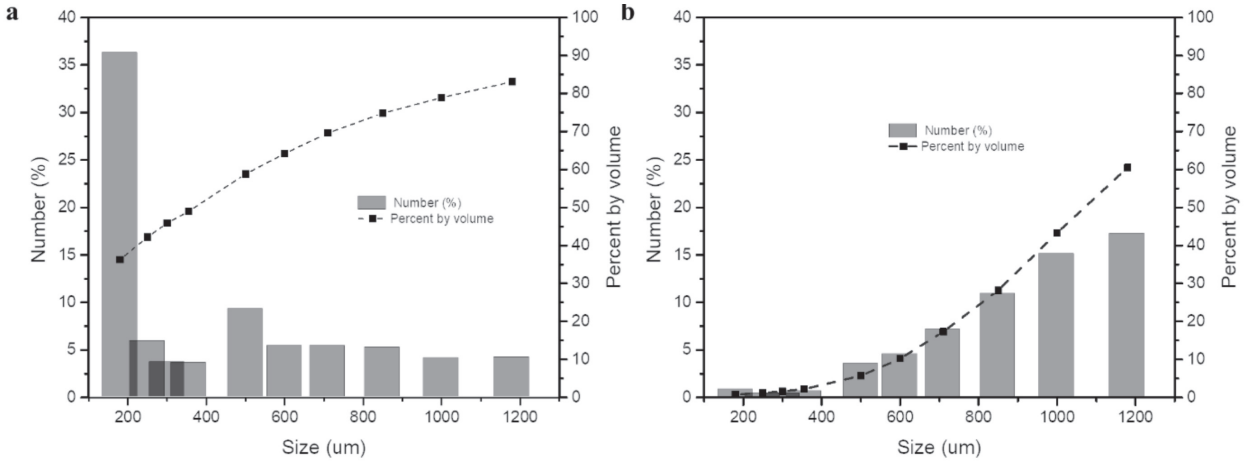

Fig. 2. Particle size distribution (PSD) for BA (*a*) and GAC (*b*).

(2016) for biochar generated from agricultural wastes.

With regard to the pore properties, a lower surface area was determined for BA (194 m^2/g) than for GAC (211 m^2/g). Similarly, the average pore diameter and the ratio of mesopore volume to total volume of BA were lower compared to GAC. However, these values were in good agreement with those reported by Simaratanamongkol and Thiravetyan (2010), who classified the cavities of activated carbon from BA as mesopores and found the material suitable to remove synthetic melanoid in with a molecular weight of 15,000 Dalton from aqueous solution.

N_2 adsorption and desorption isotherms for both materials investigated in this work are presented in Fig. 3. The isotherms of BA were found to correspond to Type 1, while the isotherms of GAC were Type 2 according to the IUPAC classication. This indicates that BA is a microporous adsorbent while GAC is classified as mesoporous Aworn *et al.* (2008).

The FTIR spectra for BA and GAC presented in Fig. 4 show the presence of four notable common peaks for both BA and GAC (at 1,566, 1434, 1,099 and 877cm^{-1}), whilst two peaks were detected only in the BA spectrum (3,344 and 467cm^{-1}). Concerning the latter, we hypothesize that the broad band at~3,344 cm^{-1}in BA may be due to the presence of –NH_2 groups (Aneja *et al.*, 2015). The weak signal at

Table 1. Physical properties, chemical properties and ultimate analysis of BA and GAC.

	BBA	**GAC**
Proximate (dry basis)		
Volatile matter (%)	16.81	13.28
Fixed Carbon (%)	45.77	77.04
Ash (%)	37.42	9.68
Elemental (dry basis)		
Carbon (%)	47.02	68.13
Hydrogen (%)	2.04	1.89
Nitrogen (%)	0.30	0.70
Sulfur (%)	0.03	0.25
Physical and chemical properties		
Total surface area, S_{BET} (m^2/g)	194	211
Total pore volume, V_T (cm^3/g)	0.145	0.260
Mesopore volume, V_{me} (cm^3/g)	0.077	0.220
Micropore volume, V_{mic} (cm^3/g)	0.068	0.040
Mesopore proportion (%) (V_{me}/V_T)	53.3	84.6
Average pore diameter, D_P (nm)	2.99	4.93
Average diameter(D_n) (µm)	364	1062
Coefficient of variation (CV)	160	38
Bulk Density (g/cm^3)	0.15	0.67

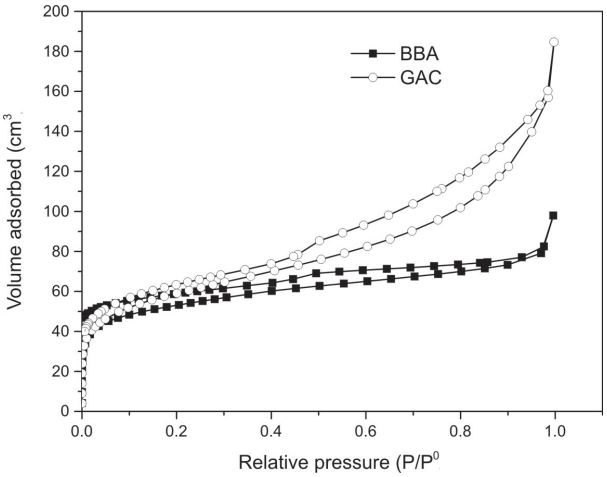

Fig. 3. N_2-adsorption–desorption isotherm of BA and GAC

1,566 cm^{-1} in both materials may be caused by the asymmetric stretching vibration of –NO_2 (Udhayakala *et al.*, 2011), while the small peak at 1,434 cm^{-1} in the spectra of both adsorbents may be related to C=C stretching (Rodríguez-Díaz *et al.*, 2015). The strongest vibration of BA and the weak peak in the range of 1,099-1,077 cm^{-1} is assigned to –O–Si–O– stretching modes (Govindarajan and Jayalakshmi, 2011). The small peak ~870 cm^{-1} can be designated to Si–OH bonds or Al–OH bonds (Moisés *et al.*, 2013) and the low signal at 467 cm^{-1} of BA is assumed to correspond to the Si–O–Si bending mode (Govindarajan and Jayalakshmi, 2011; Sanaeishoar *et al.*, 2015).

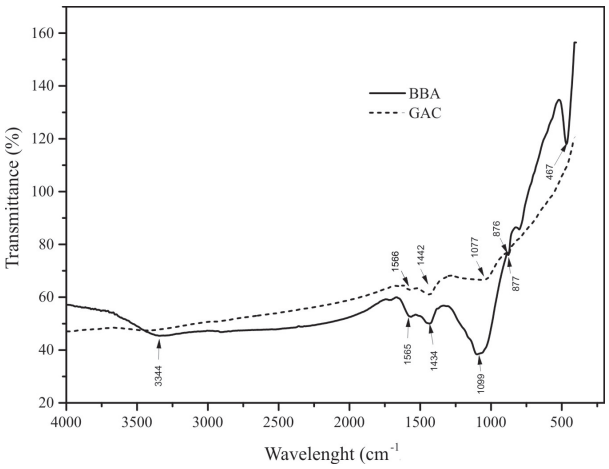

Fig. 4. FTIR spectrograms of BA and GAC.

Representative SEM images for BA at 100x and 500x magnification are shown in Fig. 5. The surface of BA displays rectangular and circular structural characteristics (Fig. 5a) which is typical of the

cellular structure of sugarcane. The porosity of BA is clearly visible in Fig. 5-b with similar morphologies also being reported in previous studies (Shah *et al*., 2011; Rodríguez-Díaz *et al.*, 2015; Taha *et al.*, 2016). The porosity in the surface of BA may be involves the pathway of adsorbate molecules towards inside the adsorbent for adsorption.

Effect of flow rate on the decolorization of brine wastewater

The flow rate of the influent is an important parameter affecting the adsorption process. The effect of BWW flow rate variation in the range of 120-460 mL/min on the colour removal with BA at a bed depth of 35 cm and initial $OD_{420\ nm}$ of 2.0 is shown in Fig. 6. It can be seen that equilibrium was reached at approximately 400 min, 260 min and 120 min for flow rates of 120 mL/min, 230 mL/min and 460 mL/min, respectively. The designated target decolorization or the breakthrough point in this research was defined as 60% or C_t/C_0= 0.4 (Ngasan *et al*., 2019). It was noticed that the time required attaining equilibrium decreased with increasing flow rate. The effluent volumes after passing through the BA column at the breakthrough point at a flow rate of 120, 230 and 460 mL/min was 14.9, 20.0 and 19.3 L, respectively (Table 2).

Effect of bed depth on the decolorization of brine wastewater

The influence of changing the bed depth to either 35, 70 or 140 cm on the colour removal with BA at an initial OD_{420nm} of 2.0, and a flow rate of 120 mL/ minis highlighted in Fig. 7. The results show that a bed depth of 140 cm gave the highest equilibrium time of 30 h. The effluent volumes after passing

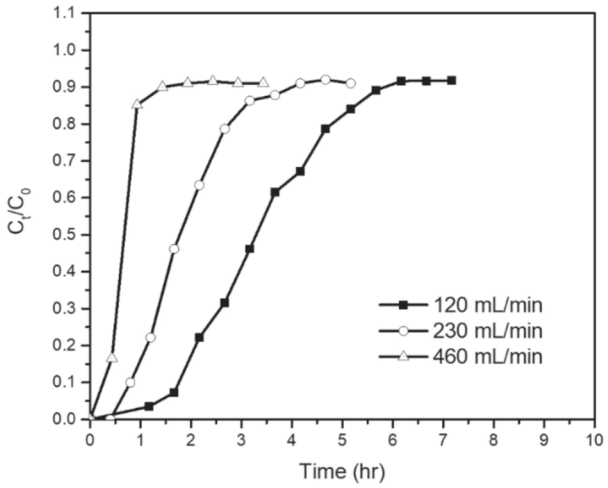

Fig. 6. The effect of flow rate on breakthrough curve (bed depth of 35 cm; initial OD_{420} nm of 2.0).

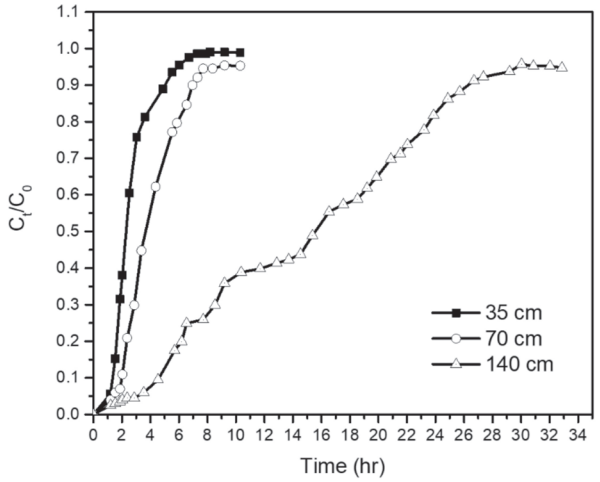

Fig. 7. The effect of bed depth of BFA on breakthrough curve (initial OD_{420} of 2.0 and flow rate of 120 mL/ min).

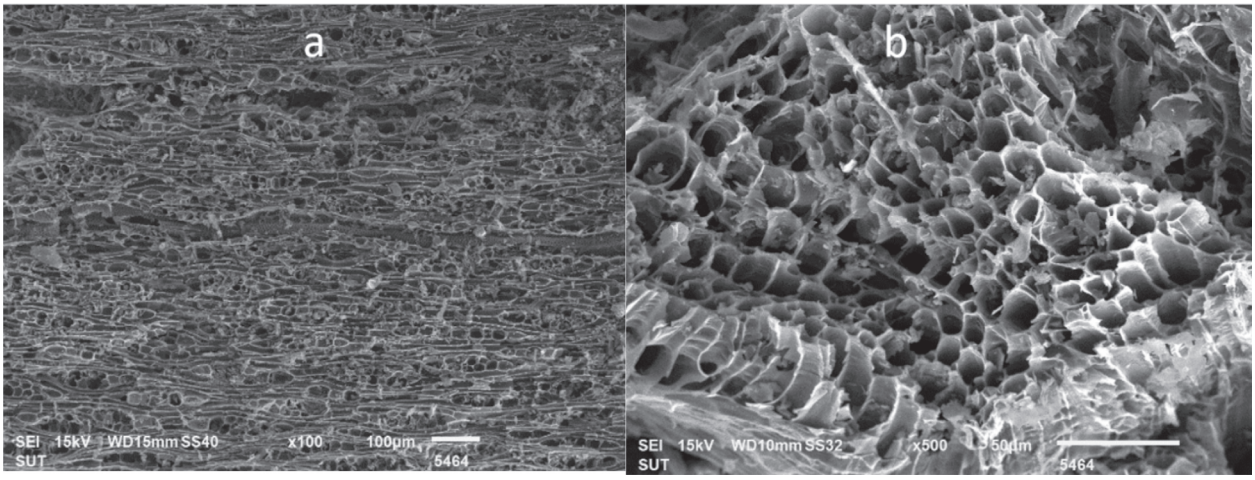

Fig. 5. SEM images of BA at × 100 (a), and x500 (b) magnification.

through the BA column at the breakthrough point of bed depth of 35 and 140 cm were 14.6 and 84.2 L, respectively (Table 2). This corresponds to a5-fold increase of equilibrium time and the effluent volumes when increasing the bed depth from 35 cm to 140 cm, presumably due to the greatly amplified contact time between color pigments in BWW and BA.

Effect of the influent $OD_{420\ nm}$ of brine wastewater on decolorization

Investigation of the effect of initial color (OD_{420nm}) of BWW on the breakthrough curve was performed using BA at a 35 cm bed depth and a flow rate of 120 mL/min. The extent of BWW discoloration was found to have a pronounced effect on the color adsorption (Fig. 8), resulting in BWW with an initial color value of 7.0 a.u. to exhibit the lowest breakthrough time (Table 2). Overall, however, the result indicated that it was possible to achieve low colorant concentration in the treated BWW samples (< 2 a.u.), thus suggesting that BA represents asuitable adsorbent for BWW treatment.

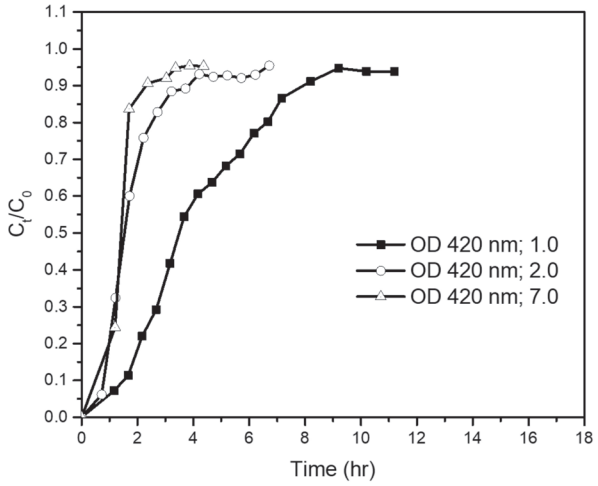

Fig. 8. The effect of initial color of BWW on breakthrough curve (bed depth of 35 cm, flow rate of 120 mL/min).

Efficiency of brine wastewater decolorization by BA and GAC

The decolorization efficiency and the characteristics of treated BWW were studied by comparison between BA and commercial GAC-based adsorption. Therefore, experiments were conducted at a flow rate of 120 mL/min, with an adsorbent bed depth of 140 cm and at room temperature. The initial $OD_{420\ nm}$ of BWW was controlled by water addition until an $OD_{420\ nm}$ of ~1.7-1.9 units were achieved, while the target remaining color in the effluent was defined as an OD_{420nm} of 0.8. Comparison of the measured residual color of the effluent samples (Fig. 9) and the column data (Table 3) shows that BA had a lower decolorization efficiency than GAC. The effluent volumes from BA and GAC adsorption required to obtain the target color ($OD_{420\ nm}$ of 0.8) were 36 and 157 L/kg of adsorbent, respectively, corresponding to a maximum adsorbent dosage of 5.56% w/v BA. Notably, the required amount of adsorbent in the current study was lower than the on ereported by Ngasan *et al.* (2019) who determined a maximum treated fly ash dosage of 12% w/v to be necessary in order to reach the set target decolorization threshold. This result can be explained by differences in the properties of the utilized adsorbents; specifically, the significantly lower mesopore volume and surface area of BA compared to GAC (Table 3). Support for this explanation can be found in previous work from Pendyal *et al.*, (1999), who suggested that the high color

Table 2. The influence of flow rate, bed dept and initial $OD_{420\ nm}$ on decolorization of BWW using BA.

Flow rate (mL/min)	Adsorbent (kg)	Bed depth (cm)	Initial Color ($OD_{420\ nm}$)	Tb at C_t/C_0 =0.4 (h)	Amount adsorbed at Tb (L)	Amount adsorbed at full bed exhaustion (L)
120	0.5	35	1.99	2.9	14.9	47.5
230	0.5	35	2.00	1.45	20.0	59.3
460	0.5	35	2.00	0.7	19.3	69.0
120	0.5	35	1.97	2.0	14.6	39.8
120	1.0	70	2.00	3.2	23.1	52.6
120	2.0	140	2.00	11.7	84.2	192.2
120	0.5	35	1.11	4.2	30.6	66.2
120	0.5	35	2.00	1.9	14.0	51.8
120	0.5	35	7.17	1.3	9.6	21.8

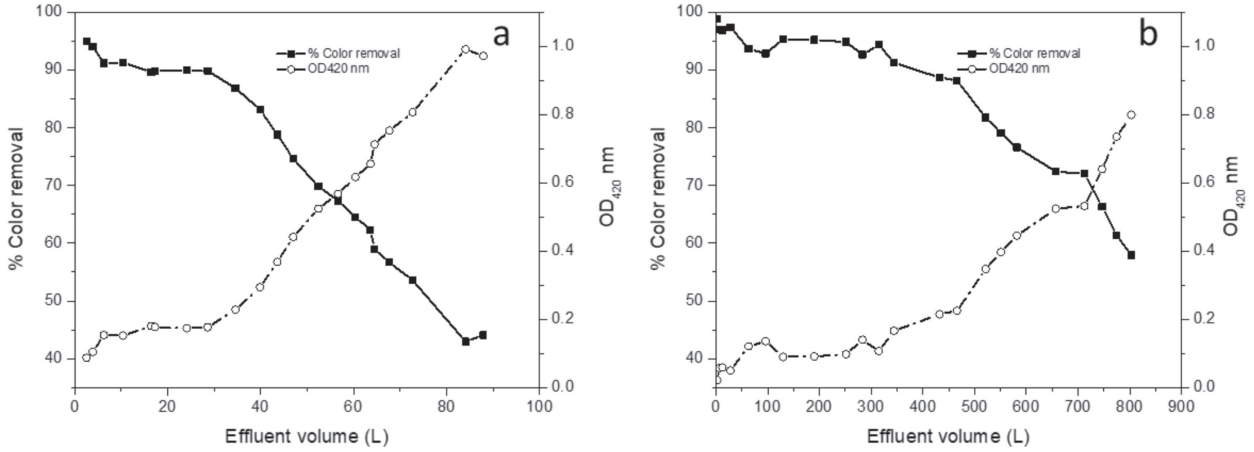

Fig. 9. Color removal from BWW by BA (a) and GAC (b) using 140 cm bed depth of adsorbents, flow rate of 120 mL/min.

adsorption efficiency of activated carbon can be attributed to the high surface area and mesopore volume of such adsorbents. The colorants in BWW originate from the fine syrup produced during the sugar refining process and are adsorbed by the resin matrix, from where they are subsequently eliminated by 10-12% sodium chloride under caustic conditions (Jahed *et al.*, 2014). After regeneration, the effluent containing high colorant levels is sent to the nano filtration system (NF). Colorants with high molecular weight partition into the retentate or BWW (Rein, 2007), due to the fact that large molecules in BWW would have difficulty entering the micropores and thus would exhibitlimited adsorption (Pendyal *et al.*, 1999).

The distribution of colorants in the effluent was monitored via their respective indicator values (I.V.). Therefore, filtrated samples from the breakthrough studies were adjusted to pH 4.0 and pH 9.0, before measuring the difference in absorbance at 420 nm. It was found that high molecular weight (MW) colorants exhibit a low I.V., while low MW colorants show high I.V. values (Table 4). The colorants in the effluent following GAC adsorption were found to be of low MW at the beginning, i.e. with an I.V. = 7-13 at 1-3 h indicative of Phenolics and Flavonoids as the major constituents, whereas high MW colorants (melanoidins or caramels) dominated near the breakthrough point. The results indicate that GAC is capable of adsorbing high MW substrates initially and low MW substrates close to the breakthrough point (Fig.10b), while BA adsorption displayed atendency to adsorb low MW compounds exclusively (Fig. 10a). Notably, these results allow correlation of the measured pore properties with the observed decolorization efficiency. It is inferred that

Table 3. Column parameters for BWW decolorization by BA and GAC and their properties.

Adsorbents	C_0	W (kg)	T_s (h)	V_{eff} (L)	% DE	C_t
BA	1.74	2.0	20	73	54	0.81
GAC	1.90	5.1	116	803	58	0.80

Note: C_0: initial color ($OD_{420\ nm}$), W: Weight, T_s: Service time, V_{eff}: Effluent volume, DE: Decolorization efficiency, C_t: final color ($OD_{420\ nm}$).

Table 4. Relationship between indicator values and molecular weight ranges of common colorants in BWW (Smith and Gregory, 1971; Clarke *et al.*, 1987; Bento, 2009, Davis, 2001)

Colorants	Indicator Value (I.V.)	Molecular weight (MW)
Melanoidin	1.0 – 1.2	>2500
Caramel	1.0 – 1.5	>2500
Fructose alkaline degradation products	1.5 – 3.2	1000 - 2500
Phenolics and flavonoids	5.0–40.0	<1000

the high molecular weight fraction of colorants present in BWW can get entrapped in themes pores of GAC, while the microporous structure of BA is more suitable for adsorbing colorants with low molecular weight.

The pH, EC, COD, turbidity and % Brix measured both before and after treatment of BWW bypassing through either the BA or GAC column were analyzed and compiled in Table 5. The pH value of BWW increased from 4.76 to 7.57 and 4.75 to 6.62 after treatment using the BA and GAC adsorption column, respectively. These results indicate that transfer of ions from the adsorbent to the effluent water was higher in case of BA than for GAC. The EC of BWW following both treatments was reduced by approximately 25-28% compared with fresh BWW. Treatment using the GAC column resulted in the removal of 58.6% COD whilst the BA column only displayed a COD removal of 12.9%. The reason for this discrepancy may be due to the enhanced mesopore volume and surface area of GAC compared to BA (Devi *et al.*, 2008). The

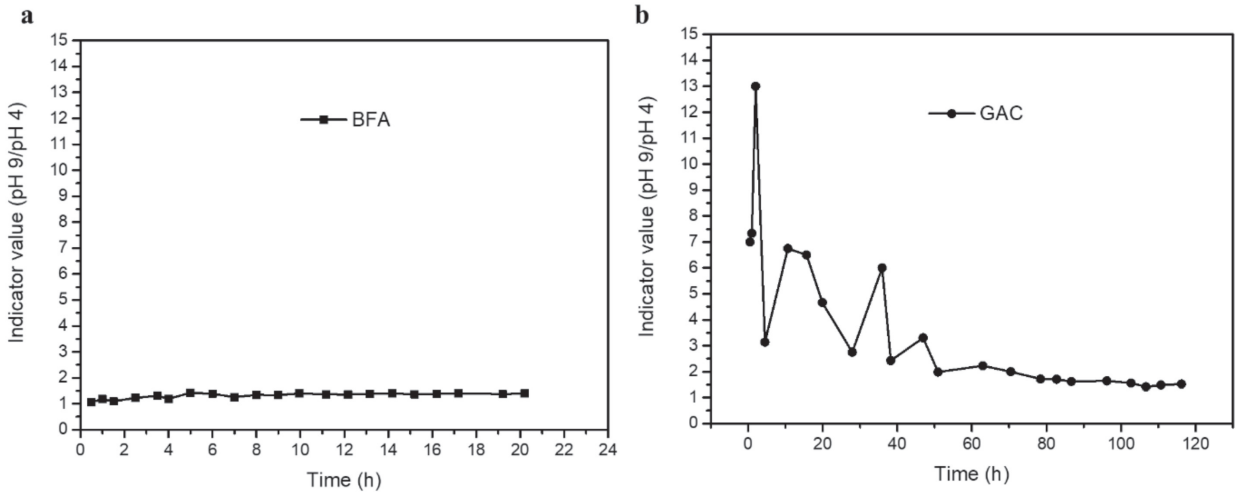

Fig. 10. Indicator value of effluent samples from fixed bed column using BA(*a*) and GAC (*b*).

Table 5. Characteristics of BWW before and after treatment using BA and GAC at the breakthrough point

Parameters	pH	EC (μS/cm²)	COD (mg/L)	Turbidity (%)	Brix (%)
Before treatment with BA	4.76±0.02	45.27±1.00	14,137±51.32	0.59 ±0.09	4.07±0.09
After treatment with BA	7.57±0.04	33.54±2.77	12,313±30.55	0.65±0.06	3.02±0.25
Before treatment with GAC	4.74±0.02	45.67±1.52	8,599±59.55	0.63±0.05	4.11±0.14
After treatment with GAC	6.62±0.01	32.65±1.98	3,557±20.07	0.66±0.19	2.94±0.18

Table 6. Metal ion concentration in the adsorbent (BBA), BWW before and after treatment using BA at the breakthrough point

Samples	BA	BWW before	BWW after
Ca (mg/L)	11,135.42 ±131	4.21±1.0	4.28±0.14
Mg (mg/L)	3,153.77 ±308	1.78±0.1	1.69±0.05
K (mg/L)	1,007.09 ±23	1.94±0.5	2.03±0.02
Na (mg/L)	1,298.48 ±141	62.83±17.6	56.58±9.84
Hg (mg/L)	0.00	0.00	0.00
Al (mg/L)	0.00	0.00	0.00
As (mg/L)	0.00	0.00	0.00
Cr (mg/L)	0.00	0.00	0.00
Cu (mg/L)	32.01 ±1	0.00	0.00
Fe (mg/L)	3,631.89 ± 164	0.00	0.00
Mn (mg/L)	331.69 ± 21	0.00	0.00
Pb (mg/L)	0.00	0.00	0.00
Zn (mg/L)	43.42 ±11	0.00	0.00

turbidity and % Brix of BWW after being treated with BA and GAC column showed the same trend. The % Brix decreased compared with untreated brine wastewater. However, the small increase of turbidity may indicate the release of some fine carbon particles from the BA into the treated brine sample. The pH, EC and COD values recorded after adsorption with both adsorbents were in good agreement with those reported for laboratory scale utilization of fly ash for BWW treatment (Ngasan, 2019).

Elemental composition of untreated and BA-treated wastewater

The migration of metal ions from BA into BWW was monitored, which allowed for the quantitation of metal content both before and after color adsorption by BA. The results showed that no aluminum, arsenic, chromium, copper, iron, manganese, lead, and zinc were found in the BWW. The calcium, magnesium and sodium concentration in treated water was found slightly decreased (Table 6), suggesting that this column material can be used for wastewater treatment without partition of heavy metal ions from the adsorbent into the brine solution. However, the fixed bed column should be coupled with membrane filtration to remove the fine particles from the treated wastewater before recycling (Ngasan *et al.,* 2019).

CONCLUSION

The physical and chemical properties of bagasse bottom ash were analysed and compared with those of granular activated carbon, revealing BA to differ from the commercial activated carbon sample in several important chemical characteristics. In particular, BA was found to contain less fixed carbon (45.8%) than GAC (77.0%), while the ash content of BA (37.4%) was higher than that of GAC (9.7%). The average diameter, surface area, mesopore volume, and bulk density were calculated as 364 μm, 194 m^2/g, 0.077 cm^3/g, 0.15 g/cm^3 for BA, respectively, and 1,062 μm, 211 m^2/g, 0.22 cm^3/g, 0.67 g/cm^3 in case of GAC, respectively. However, BA demonstrated good adsorbent properties in conducted fixed bed column studies. Pilot scale fixed bed experiments identified to be 120 m^3/min the most suitable influent flow rate, while at the maximum bed depth and full column capacity, equivalent toa column loading of 2 kg BA, the best decolorization performance was achieved. The fixed bed column using BA for BWW treatment showed the possibility to achieve low colorant concentration in the treated BWW samples (<2 a.u.). Comparison between the decolorization efficiency of BA and GAC indicated a slightly inferior performance of BA, as evident from the required effluent volumes of 36 and 157 L/kg to reach the designated target colour threshold ($OD_{420\ nm}$ of 0.8) with BA and GAC as the adsorbent, respectively. The COD removal capacity of BA and GAC was determined as 248 and 2,241 mL/L per one kilogram of adsorbent, respectively. The characteristics of the treated BWW after passing through the BA column demonstrate the potential use of this adsorbent for the decolorization of effluents in the brine recovery process, it is anticipated to facilitate the recovery and reuse of salt and, in turn, to reduce the salt and water consumption at an industrial scale.

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